

boundaries in a very curious manner. These pseudo-boundaries are often polygonal in form, like the real boundaries, and have an intimate geometrical association with them. Under low powers they are in some instances difficult to distinguish from true boundaries; but the distinction is apparent under high powers, and it becomes obvious as soon as slip-bands are developed by the straining of the metal. The pseudo-boundaries are found to consist in small variations of level in the surface of the grains in which they occur. Their form suggests that they are projections upon the surface of real edges below. They occur very conspicuously in cadmium, especially when it is cast on a cold surface, and less conspicuously in zinc. It is probable that in the strain set up by unequal cooling after the metal has solidified, the lower edges of the crystalline grains project a sort of image of themselves on the surface by slips, or possibly by narrow bands of twinning. The effect resembles that of a Japanese "magic" mirror, in which slight inequalities of the surface, corresponding to a pattern behind, cause light reflected from the mirror to produce an image in which a ghost of the pattern may be traced.

The authors regard their experiments as establishing the conclusion briefly stated in their previous paper, to the effect that the plasticity of metals is due to the sliding over one another of the crystalline elements composing each grain, without change in their orientation within each grain, except in so far as such change may occur through twinning.

"The Yellow Colouring Matters accompanying Chlorophyll, and their Spectroscopic Relations." By C. A. SCHUNCK. Communicated by EDWARD SCHUNCK, F.R.S. Received April 20, —Read May 18, 1899.

[PLATE 6.]

The yellow colouring matters dealt with are those accompanying chlorophyll in healthy green leaves and which are extracted along with it by means of boiling alcohol.

This group of yellow colouring matters is generally known by the name xanthophyll, a term first used by Berzelius, who was the first observer to express the belief that a yellow colouring matter pre-exists along with the green colouring matter in alcoholic extracts of green leaves. The subject has subsequently received the attention of many investigators—Fremy, Michels, Millardet, Müller, Tinisnaseff, Gerland, Raunenhoff, Askenasy, Stokes, Sorby, Tschirch, Kraus, Filhol, Hansen, and Schunck. The principal results arrived at by these investigators are as follows:—Filhol noticed that by treating crude alcoholic chlorophyll solutions with animal charcoal it is possible to



remove the green constituent of the mixture when a yellow coloured solution remains, the colour of which he believes is evidently due to a pre-existing colouring matter or matters associated with the green one. Kraus—to whom we are indebted for a most elaborate study of the physical properties of the yellow constituent of crude chlorophyll solutions—confirmed the observations of Filhol, and added a number of new ones which lead, according to him, to an explanation of the absorption spectrum of crude chlorophyll solutions which has hitherto been universally accepted as the correct one. The author used amongst other methods, for the purpose of separating the yellow colouring matters from the green, their different solubility in alcohol and benzol or, correctly speaking, benzoline. An alcoholic solution of chlorophyll, treated with benzoline, retains, according to him, the yellow colouring matter or mixture of colouring matters, while the benzoline takes up the green constituent. By an investigation of the spectroscopic properties of these solutions, compared to the original one, Kraus arrived at the result that the ordinary chlorophyll spectrum, which has been described with considerable accuracy already by Brewster, is a complex one, *i.e.*, that some of the absorption bands are due to the green constituent and some to the yellow. The former, he says, is characterised by six bands, four of which (comprising the well-known chlorophyll spectrum) are situated between the solar lines B and E; the fifth between F and G, and the sixth in front of G. The yellow constituent shows two bands, one at F or just behind it, and the second in front of G. These observations, according to Kraus, explain the constitution of the spectrum of crude chlorophyll solutions, the first four bands of which being due solely to the green constituent, the fifth to the yellow, and the sixth to a combination of the sixth band of the green constituent and the second of the yellow. The fifth band of the green constituent being very faint, and situated between the fifth and sixth bands of the mixture, does not, according to him, appear at all. These explanations, however, as will be shown, are erroneous.

Sorby using carbon bisulphide as the separator in place of benzoline states that along with chlorophyll in the crude alcoholic extracts of the green leaves of the higher plants there are three accompanying yellow colouring matters present which he names orange xanthophyll, xanthophyll, and yellow xanthophyll, each showing a couple of bands in slightly different positions in the more refrangible visible portion of the spectrum, but none in the less refrangible part, and also that there are other yellow colouring matters present, which he groups under the term lichnoxanthine, which obscure the more refrangible portion but exhibit no bands. He also states that chlorophyll (the green constituent) of the higher plants is separable by the same means into two colouring matters which he terms "Blue Chlorophyll" and

“Yellow Chlorophyll,” the former being the chief constituent, the latter being present in only a small relative quantity, and each give a series of bands situated throughout the visible portion of the spectrum.

Hansen’s method of isolating the yellow colouring matters is different from those of the previous observers. He treats the alcoholic extracts of green leaves with caustic alkali, evaporates the liquor to dryness, and extracts from the residue the yellow colouring matter by means of ether, the study of which lead him to believe that the yellow constituent shows only two bands.

Schunck obtains from all crude alcoholic chlorophyll extracts minute sparkling red crystals which are deposited on standing, and to which he has not applied a name, but which he considers identical with the erythrophyll of Bougarel and the chrysophyll of Hartsen. On dilution the yellow solutions of these crystals gave two absorption bands in the more refrangible portion of the spectrum, but none in the less refrangible, and, though not in the same positions as the similar bands (the fifth and sixth) shown by crude chlorophyll solutions, he considers these latter bands not due to chlorophyll but to an accompanying yellow colouring matter.

Finally, Tschorch, who used Hansen’s method for separating the yellow from the green constituent, describes two yellow colouring matters, to which he gives the names xantho-carotin, showing three bands in the more refrangible part of the spectrum and to which, according to him, the bands in the blue and violet shown by crude chlorophyll solutions are due, and xanthophyll proper, which shows no bands whatever but only a total obscuration in the violet region.

It will be seen that the results obtained by the various observers do not agree, and a renewed study of the yellow constituent of crude chlorophyll solutions appeared to be desirable. My own results differ in many respects from the hitherto generally accepted ones; they relate not only to the physical nature of the yellow colouring matters in question, but also enable us to characterise chlorophyll proper in a different manner than was possible before. The preparation of pure chlorophyll seems to baffle all attempts, but so far the physical properties of this substance, the knowledge of which would guide an experimenter in reaching the goal have, as it proves, not been known with sufficient completeness.

I will now give the results of the experiments I have made, in the endeavour to separate these yellow colouring matters from the accompanying chlorophyll, dealing more especially with their spectroscopic relations as compared to those of chlorophyll in the violet and ultra-violet region of the spectrum investigated by aid of photography—a means which, with the exception of Tschorch, former observers have not applied—and by which means I have been able to ascertain one or two new facts, and have, I think, been able to clear up the much

debated point whether the absorption bands in the violet and ultra-violet region shown by crude chlorophyll solutions are due to chlorophyll itself or to the accompanying yellow colouring matters.

The chlorophyll solutions experimented upon were obtained in the usual manner by extracting the colouring matter from the leaves with boiling alcohol. I have already shown* that chlorophyll solutions prepared in this way show three characteristic absorption bands on proper dilution, in the violet region of the spectrum, giving in the less refrangible region the well-known spectrum of four bands which in very pure solutions may be said to be reduced to three, so faint does the fourth band appear.

If the extracts are concentrated enough one finds invariably on standing for a day or so minute sparkling red crystals deposited on the sides of the containing vessel or along with the fatty deposit, coloured green by chlorophyll, which generally comes out of the extracts on standing. These crystals are found in variable quantities, but more often than not in a minute quantity.

This is the first yellow colouring matter one comes across and is the erythrophyll of Bougarel, and the chrysophyll of Hartsen and Schunck.† That chrysophyll is always to be found in chlorophyll solutions proves that either it pre-exists as such along with chlorophyll in its alcoholic extracts, or that it is formed spontaneously from one of the colouring matters, and is not, according to Hansen,‡ formed under certain conditions *only* by the decomposition of a derivative. Chrysophyll thus obtained is not a very stable substance, and in order to preserve it unchanged it should be placed in a glass tube through which a current of hydrogen has been passed before sealing, and kept in the dark. Its alcoholic solutions are bleached rapidly when exposed to the air and sunlight, and even when kept in the dark a change very soon takes place in its solutions as shown by its spectrum, though there is no apparent change in colour. According to Arnaud§ it is identical with carotin. Chrysophyll gives no absorption bands in the red, yellow, or green, but three very distinctive bands in the violet region of the spectrum which, as I have shown,|| are almost identical in position with those of carotin. They (Plate 6, fig 5) occupy intermediate positions compared to the three bands shown by crude chlorophyll solutions in the same region, being shifted more towards the red end of the spectrum.

The method I have applied for separating the other accompanying yellow colouring matters from the chlorophyll is that of treating the

* 'Roy. Soc. Proc.,' vol. 63, p. 333.

† 'Roy. Soc. Proc.,' vol. 44, p. 449.

‡ 'Die Farbstoffe des Chlorophylls,' 1889, p. 58.

§ 'Compt. Rend.,' vol. 102, p. 1119, and vol. 104, p. 1293.

|| 'Roy. Soc. Proc.,' vol. 63, p. 393.

crude alcoholic extracts with an excess of animal charcoal in the cold for about an hour, which removes all the chlorophyll and leaves a yellow solution, which gives no absorption bands in the red, yellow, or green, but four distinctive bands situated in the violet and ultra-violet region of the spectrum. The prolonged action of animal charcoal has the effect of ultimately absorbing all the colouring matters, leaving the solution colourless. By this means the yellow colouring matters can be obtained free from chlorophyll, but I have not been able to recover the latter from the animal charcoal. This was tried by boiling the charcoal with ether, the result being a greenish-yellow solution, giving the four bands in the violet as before, but, in addition, a faint band in the red, showing that it consisted of a portion of the yellow colouring matters which had been absorbed by the charcoal together with a trace of chlorophyll which caused the greenish colour, and the faint band in the red region of the spectrum.

Yellow solutions obtained in this way from some chlorophyll extracts—which, when freshly prepared, show signs of decomposition, viz., the fourth band in the visible region of the spectrum darker and the third fainter—show only the first two or three bands in the violet region, the rest of the violet and ultra-violet being obscured. In such cases a separation can be effected by ether, the yellow colouring matter causing the obscuration remaining in the alcoholic portion, the yellow ethereal portion now showing the four-banded spectrum as before. This colouring matter causing obscuration no doubt belongs to the lichnoxanthine group of Sorby,* and corresponds to the so-called xanthophyll of Tschirch.† These yellow solutions deposit on spontaneous evaporation an amorphous substance impregnated with much fatty matter, which so far I have failed to remove and have been unable to get in a crystalline form. It is insoluble in water, but easily soluble in alcohol and ether, giving as before the distinctive spectrum of four absorption bands in the violet and ultra-violet, but *no* bands in the red, yellow, or green; these bands, with the exception of the first, which is almost if not quite identical in position with the first band shown by crude chlorophyll solutions in the violet region, are in distinctly different positions to the two remaining chlorophyll bands, or the three due to chrysophyll (figs. 1 to 5). It appears to be much more stable than chlorophyll, resisting the action of light and air to a greater extent; even from crude chlorophyll solutions which have been kept for some time and show distinctly from their spectra the formation of phyllocyanin, it can be obtained unaltered by the action of animal charcoal. The solutions, when exposed to sunlight, gradually become colourless, but at a less rapid rate than those of chrysophyll, and apparently without the formation of products of decomposition, as is the

* 'Roy. Soc. Proc.,' vol. 21, p. 462.

† 'Ber. der Deutsch. Bot. Ges.,' vol. 14, part 2, p. 76. 1896.

case with chlorophyll; while away from the light it can be kept for a considerable time without any apparent change taking place in its solutions. Alkalies which induce so great a change in chlorophyll appear to have no action upon it. From chlorophyll solutions which have been boiled with potash or soda, and from which animal charcoal will not now absorb any appreciable amount of colouring matter, ether takes up this yellow colouring matter unaltered. Likewise, if its alcoholic solutions be boiled with an alkali, no alteration is discernible. On the other hand, if hydrochloric acid gas be passed through its alcoholic solutions the colour changes to a dull dark-red, giving no bands, but a general obscuration in the violet and ultra-violet region of the spectrum. By this method I have obtained this yellow colouring matter from two species of *Ficus*, from parsnip, clover, birch, and Virginia creeper leaves, the extracts of the last-named, when even freshly prepared, showing a near approach to the phyllocyanin spectrum. I have also examined the yellow colouring matter of autumnal leaves, and find that it is identical with it both in properties and spectrum (Plate 6, figs. 3 and 4); but in autumnal leaves invariably I find the presence of the other yellow colouring matter which obscures the spectrum, but which can be got rid of by separating with ether. This supports the belief that the yellow colouring matter of autumnal leaves is what remains after the chlorophyll of the healthy green leaf has faded away, the latter being the less stable of the two (as has already been shown to be the case), and fading first. I have examined the colouring matter of some etiolated leaves, and here the presence of a yellow colouring matter that obscures the spectrum in the violet and ultra-violet region is undoubted. I endeavoured to get rid of it, as in the former experiments, by separating with ether, but seemingly with only partial success, the ethereal portion showing only three bands, but in the same positions as the first three bands of the yellow colouring matter under review, the rest of the spectrum in the violet and ultra-violet being obscured.

It is to this yellow colouring matter giving the characteristic spectrum of four bands in the violet region, a spectrum not before observed, I believe, and which I believe to be the predominating yellow colouring matter accompanying chlorophyll in ordinary green leaves, and also of faded autumnal leaves, that I would restrict the name xanthophyll, just in the same way that phylloxanthin, from being first applied by Fremy to include *all* the yellow colouring matters accompanying chlorophyll, as well as a yellowish-brown decomposition product of the latter, has been applied by Schunck in a stricter sense to one of the group only—the yellowish-brown decomposition product of the action of acids. Crude alcoholic chlorophyll solutions can, as before stated, be separated into a green and yellow portion by agitating with carbon bisulphide—Sorby's method—or by benzoline, Kraus's method, the

carbon bisulphide and benzoline portions being coloured green, and the alcoholic portion in each case yellow. I believe from the few experiments I have so far made by these methods of separation, that the xanthophyll, as I have defined it, passes along with the chlorophyll into the carbon bisulphide or the benzoline, a point overlooked by Kraus, but noticed by Sorby, while the alcoholic portion contains yet another yellow colouring matter or matters, showing ill-defined absorption bands in the violet region, but in different positions again to either the bands of chrysophyll or xanthophyll. May be we have here the xanthophyll and yellow xanthophyll of Sorby,* whilst probably my xanthophyll corresponds to his orange xanthophyll.

I hope after some further experiments by these means of separation which I am now undertaking, to be able to throw some further light upon the apparent complex nature of this group of accompanying yellow colouring matters.

The Spectroscopic Relations of Chlorophyll, Chrysophyll, and Xanthophyll.

The method of observing the absorption spectra by means of photography is the same as I adopted in a former investigation, dealing with chlorophyll and its derivatives,† quartz lenses and an Iceland spar prism being used. The question whether the bands shown by crude chlorophyll solutions in the violet region are due to chlorophyll itself, or to an accompanying yellow colouring matter, has not so far been answered in a satisfactory manner. Some observers consider them due to the former, whilst others, the majority I believe, attribute them to the latter.

On inspection of the plate (figs. 1, 2, and 5), it will be seen that the chrysophyll bands are shifted towards the red end of the spectrum compared to those of crude chlorophyll, so that if chrysophyll pre-exists along with chlorophyll in its alcoholic extracts, the bands of the two spectra would overlap, so as to produce one broad band extending from F to K_B; but in all the freshly prepared normal crude chlorophyll extracts I have examined, I have never found this to be the case, the three bands always being visible on proper dilution, with no indication of those due to chrysophyll.

We can therefore conclude that they are not due to chrysophyll, and must assume that if chrysophyll pre-exists, its relative quantity compared to chlorophyll must be small. In the xanthophyll spectrum, it will be noticed (Plate 6, fig. 3) the first three bands do not coincide with the chrysophyll bands, being shifted towards the ultra-violet, and the spectrum is further distinguished by a fourth band situated between K_B and L, which is lacking in chrysophyll, the latter having the cha-

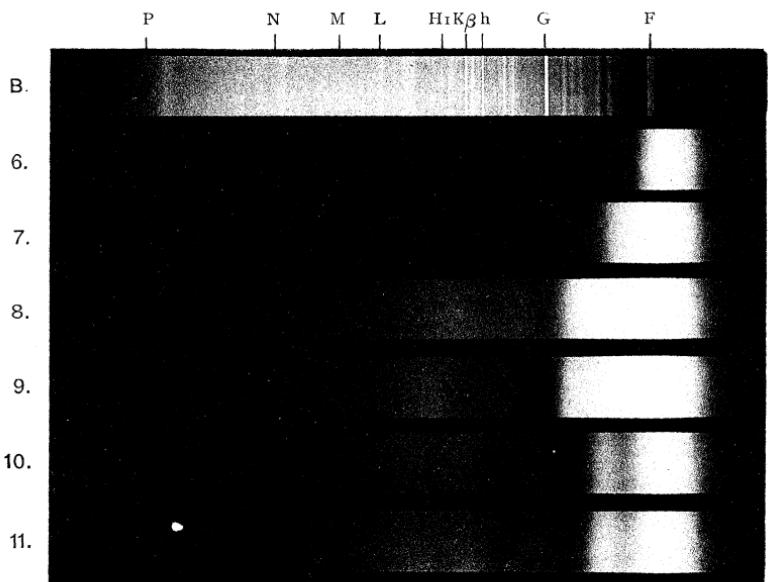
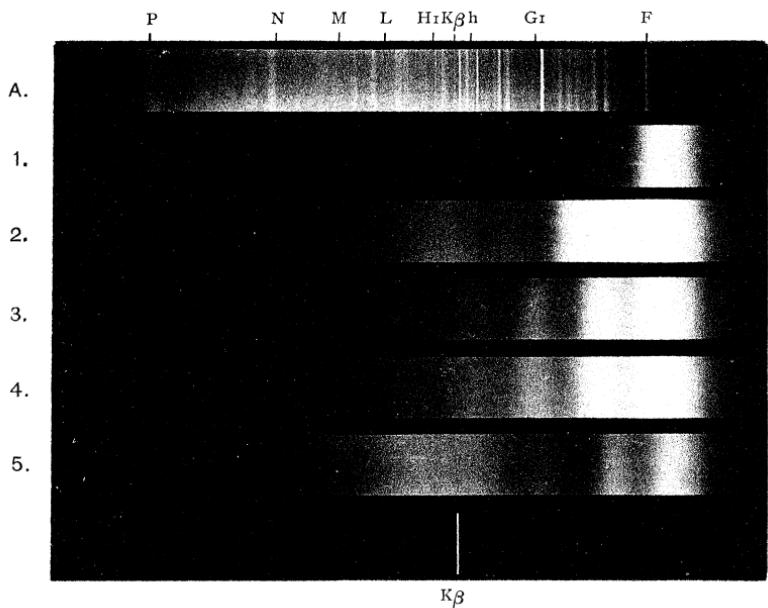
* 'Roy. Soc. Proc.,' vol. 21, p. 456.

† 'Roy. Soc. Proc.,' vol. 63, p. 391.

racteristic of allowing considerably more of the ultra-violet rays to pass through its solutions. Comparing now the xanthophyll spectrum with that given by crude chlorophyll solutions, it will at once be seen that the character of the two spectra are quite different, and this points to the fact that the bands are due to two distinct colouring matters. This is supported by the fact that from crude alcoholic chlorophyll solutions that have been acted upon with alkali, the xanthophyll can be recovered unaltered by shaking up with ether, the chlorophyll being so altered (though the colour of the solutions is unchanged) that animal charcoal will not now absorb the green colouring matter; this alteration has been shown by Schunck* to be due to the formation of an alkali compound of alkachlorophyll. Again, in crude chlorophyll solutions which have been kept a little time, and which show signs of decomposition, owing to the formation of phylloxanthin and phyllo-cyanin, the bands in the violet are no longer discernible on proper dilution, yet act upon such solutions with animal charcoal, and we get a yellow solution giving the four-banded xanthophyll spectrum, showing that the xanthophyll was there all the time unaltered, but did not affect the spectrum. From the spectra of their alcoholic solutions it will be observed the only xanthophyll band that could affect the crude chlorophyll spectrum is the first, for it is the only one in a similar position; but I think I can show that this cannot be the case, and that it is in no way connected with chlorophyll. If a crude chlorophyll solution be examined in ether compared to alcohol, it will be found that in the former solvent, the bands are all shifted towards the more refrangible end of the spectrum, while the xanthophyll bands in both solvents are in identical positions (Plate 6, figs. 6 to 11), so that we see now the first xanthophyll band no longer coincides with the first band of crude chlorophyll, and therefore can not have any influence upon the chlorophyll spectrum. And thus I came to the conclusion, taking one experiment with another, that as with chrysophyll, xanthophyll is present in such a small relative quantity, compared to chlorophyll, that the bands of its spectrum cannot be detected in the crude chlorophyll solution, and that the bands shown by the latter are due to chlorophyll itself, and not to any of the accompanying yellow colouring matters which the majority of former observers believed they were due to. This belief may have arisen from the fact that without the aid of photography, only the first two bands of chlorophyll and the accompanying yellow colouring matters in the violet region are discernible in alcoholic solutions to the eye, and they thus failed to observe the complete spectrum which, from an inspection of the plate, will be seen makes in each case a vast difference to the character of the spectrum.

That all freshly prepared chlorophyll extracts show in every case

* 'Roy. Soc. Proc.,' vol. 50, p. 312.



the three bands in the violet region, is I think a proof in itself that they are due to the same colouring matter that produces the characteristic and unmistakable spectrum in the less refrangible region, or to a *very* intimately connected colouring matter so far unknown. Seeing also that all the chlorophyll derivatives give a characteristic absorption in the violet and ultra-violet region, it would be strange that chlorophyll proper should prove the exception, and it is an interesting fact that its two chief, and intimately connected decomposition products *inter se*—phyllocyanin and phylloxanthin—should have, as I have shown,* bands in the violet region in identical positions with these three chlorophyll bands, the first of them corresponding to a faint, but distinct one, observable in pure phyllocyanin solutions on proper dilution, the other two to the two characteristic phylloxanthin bands in the violet region.

Summary.

1. I find in *all* crude alcoholic extracts of healthy green leaves, two yellow colouring matters accompanying the chlorophyll. One chrysophyll which deposits out of the extracts on standing in lustrous red crystals, but more often than not in minute quantities, the other obtained by treating the extracts with animal charcoal in the cold, the charcoal taking up the chlorophyll, and leaving a yellow solution which deposits on spontaneous evaporation an amorphous substance impregnated with much fatty matter, and to which I have restricted the name xanthophyll. Another yellow colouring matter is sometimes found along with xanthophyll which gives no absorption bands, but only an obscuration in the violet and ultra-violet region of the spectrum, and in such cases a separation can be effected by ether. There is also evidence to show that other yellow colouring matters may exist. Xanthophyll, however, I believe, is the predominating yellow colouring matter accompanying chlorophyll in the healthy green leaf, and I also find it to be identical with the principal yellow colouring matter of the faded autumnal leaves.

2. Chrysophyll and xanthophyll each give a characteristic absorption spectrum in the violet and ultra-violet region; the former consists of three bands, the latter of four, but in slightly different positions. Crude chlorophyll solutions also give, in addition to the characteristic spectrum of four bands in the less refrangible region; three characteristic bands in the violet, and from observations by means of photography I come to the conclusion that these bands are due to chlorophyll itself, and not to any of the accompanying yellow colouring matters which the majority of former observers believed they were due to. I also find that phyllocyanin and phylloxanthin have bands in identical positions with these three chlorophyll bands.

* 'Roy. Soc. Proc.,' vol. 63, p. 393.

EXPLANATION OF PLATE.

A and B. Spectrum of a hydrogen vacuum-tube from which the reference lines, F, G', h, and H₁ are obtained, with the potassium K_B line thrown in. The solar lines, L, M, N, and P are obtained by measurement from a negative of the solar spectrum.

FIG. 1. Crude chlorophyll in alcohol.

- „ 2. „ „ „ diluted.
- „ 3. Xanthophyll from crude chlorophyll solutions in alcohol by the action of animal charcoal.
- „ 4. Xanthophyll from faded autumnal yellow leaves in alcohol.
- „ 5. Chrysophyll in alcohol.
- „ 6. Crude chlorophyll in alcohol.
- „ 7. „ „ „ ether.
- „ 8. „ „ „ alcohol diluted.
- „ 9. „ „ „ ether „
- „ 10. Xanthophyll in alcohol.
- „ 11. „ „ „ ether.

“On the Chemical Classification of the Stars.” By Sir NORMAN LOCKYER, K.C.B., F.R.S. Received April 27,—Read May 4, 1899.

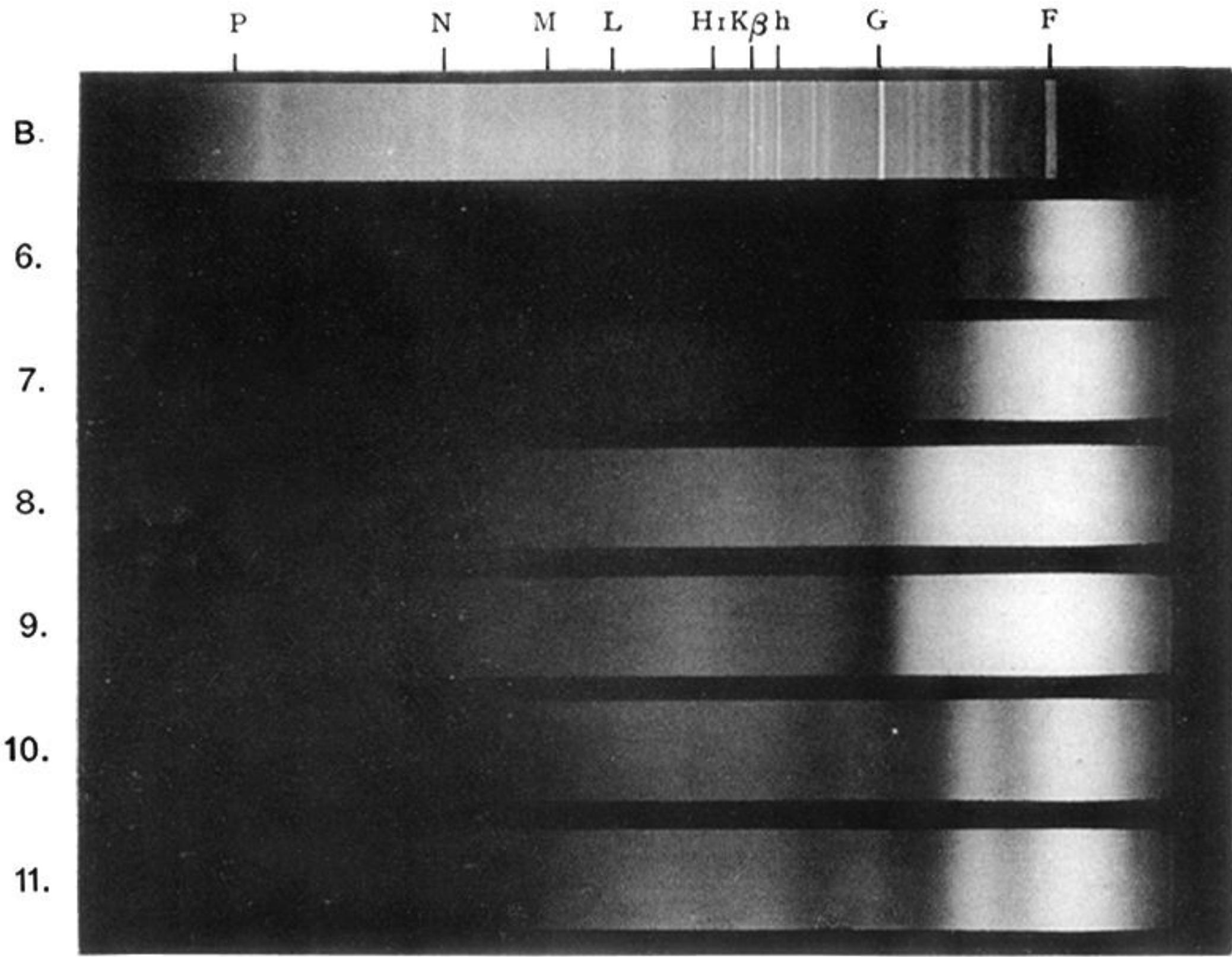
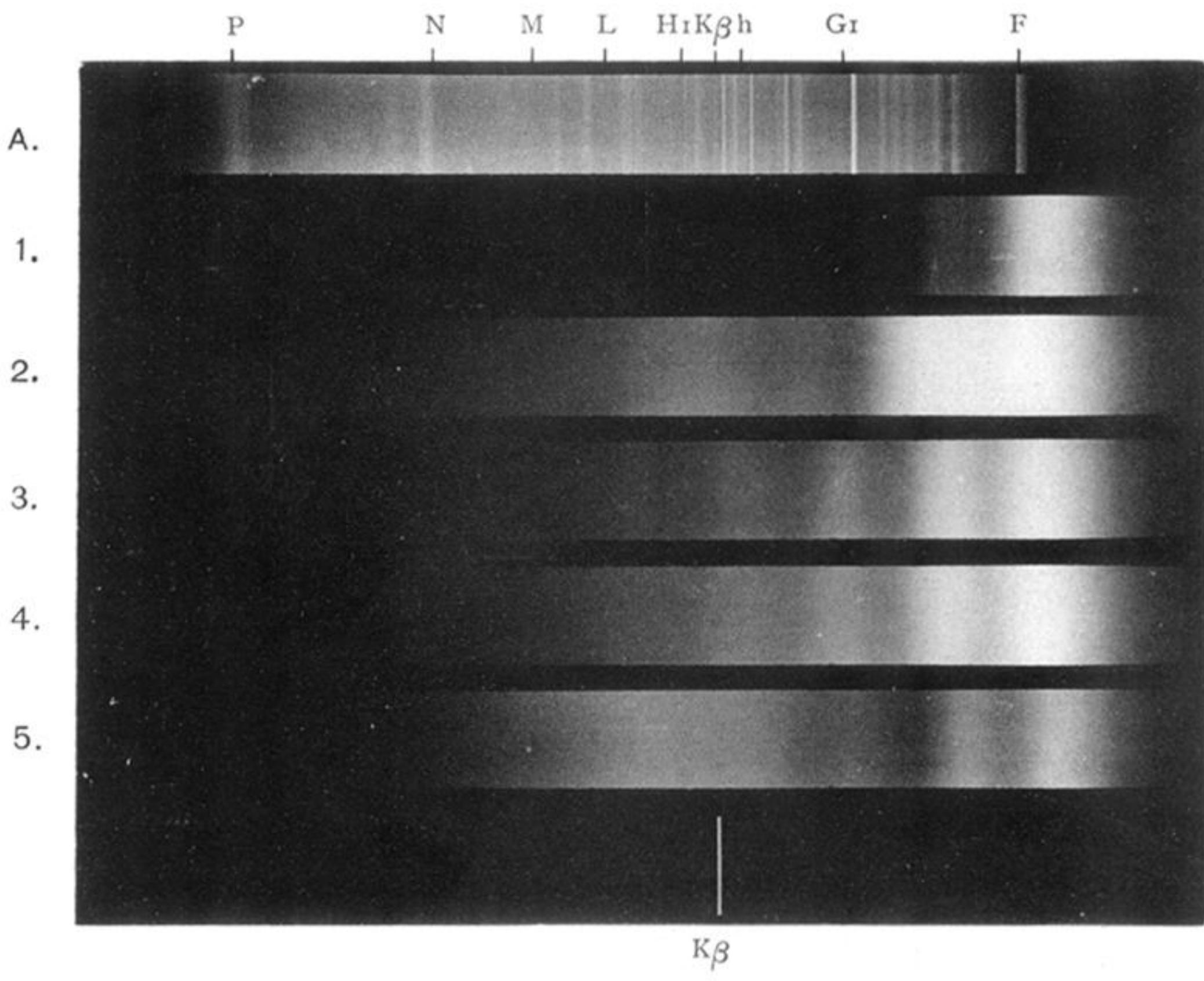
[PLATE 7.]

In the attempts made to classify the stars by means of their spectra, from Rutherford's time to quite recently, the various criteria selected were necessarily for the most part of unknown origin; with the exception of hydrogen, calcium, iron, and carbon, in the main chemical origins could not be assigned with certainty to the spectral lines. Hence the various groups defined by the behaviour of unknown lines were referred to by numbers, and as the views of those employed in the work of classifying differed widely as to the sequence of the phenomena observed, the numerical sequences vary very considerably so that any co-ordination becomes difficult and confusing.

Recent work has thrown such a flood of light on the chemistry of the stars that most definite chemical groupings can now be established, and the object of the present communication is to suggest a general scheme of classification in which they are employed, in relation to the line of cosmical evolution which I have developed in former papers communicated to the Society.

The fact that most of the important lines in the photographic region of the stellar spectra have now been traced to their origins renders this step desirable, although many of the chemical elements still remain to be completely investigated from the stellar point of view.

The scheme is based upon a minute inquiry into the varying intensities, in the different stars, of the lines and flatings of the undermentioned substances:—



EXPLANATION OF PLATE.

A and B. Spectrum of a hydrogen vacuum-tube from which the reference lines, F, G', h , and H_1 are obtained, with the potassium $K\beta$ line thrown in. The solar lines, L, M, N, and P are obtained by measurement from a negative of the solar spectrum.

FIG. 1. Crude chlorophyll in alcohol.

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- „ 9. „ „ „ ether „
- „ 10. Xanthophyll in alcohol.
- „ 11. „ „ „ ether.